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THE USE OF SULPHUR MONO CHLORIDE AS A CARRIER IN THE PRODUCTION OF ACID CHLORIDES

BY

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THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

Harry Francis Watson

ENTITLED The use of Sulphur Mono Chloride as a Carrier in the Production of Acid Chlorides

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE DEGREE OF Bachelor of Science in Chemistry

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PREFACE

The work was undertaken at the suggestion of Professor Adams in order to investigate the practical possiblilities of the method. Some of the work was done on the problem at Washington, D.C., under the direction of Professor Adams. The investigations were carried out under varing conditions; the practicability of the process being the keynote of all the work done. The two acid chlorides which were investigated were acetyl chloride and benzoyl chloride.

BIBLIOGRAPHY AND THEORETICAL CONSIDERATIONS.

A brief account is given in Bulletin de la Societe Chemque 1887, Series A, page 145 of the interaction between SCl_4 and CH_3CO_2H by V. Auger. The method followed being: A flask in which one mole of S_2Cl_2 and two moles of CH_3CO_2H was cooled with ice and salt (temperatures not given). Chlorine was passed into the mixture until no more chlorine was absorbed, when the flask was allowed to warm up to room temperature. The free sulfur compounds were removed by shaking with mercury or copper powder. The mixture was then distilled until a boiling point of 60° was reached.

The yield given was 500 grams of acetyl chloride from 600 grams of acid. No mention is made of SO_2Cl_2 in the product.

SCl_4 is only stable at -19° and at higher temperatures an equilibrium exists $SCl_4 \rightleftharpoons SCl_2 + Cl_2$.

It was thought that at 10° to 0° the reaction would probably progress smoothly without too high a formation of of the chlor compounds of the methyl group. The reactions considered were the reaction of SCl_4 present in small amounts at 0° to 10° bringing about the reaction

$$2CH_3CO_2H + SCl_4 \longrightarrow 2CH_3COCl + SO_2 + 2HCl$$

The additional possiblility of the reaction

$$2CH_3CO_2H + SCl_2 + Cl_2 \longrightarrow 2CH_3COCl + SO_2 + 2HCl$$ was considered.

Many patents have been taken out for the production of $(CH_3CO)_2O$ from CH_3COONa and S_2Cl_2 Cl_2. See Chemical Society Transactions 1909, p. 1235; 1913 p. 1361. Die Berichte 1884 p. 1286, also Thorpes Dictionary of Applied Chemistry: Acetic Anhydride, pages 27 -30, Vol. I, 1921 Edition.

The interaction of $SO_2Cl_2 + CH_3CO_2Na$ for production of CH_3CO_2Na is quite well known. A working application being given in German Patent ss6, 218, 1907.

The reaction being carried out at 20° and is as given $2CH_3COONa + SO_2Cl_2 \longrightarrow 2CH_3COCl + 2NaCl + SO_2$. In the presence of an excess of CH_3CO_2Na acetic anhydride is formed.

$$CH_3COONa + CH_3COCl \longrightarrow (CH_3CO)_2 + NaCl$$

In all the reactions employed for the production of acetic anhydride using either the S_2Cl_2 or the oxychlor compounds CH_3COCl is an intermediate compound.

Reasoning from analogy if CH_3CO_2H were used it should yield a high yield of CH_3COCl and a very little Acetic anhydride. This reasoning proved correct as is shown in the experimental work.

The production of benzyoyl chloride by the use of S_2Cl_2 and Cl_2 was investigated as a similar case. The low rate of activity found in the chlorination was probably due to too low temperature, the gum like substance was a sulfur organic compound such as are discussed in Journal of the Chemical Society 1913, page 1861. The type of compound which is unstable

is $(C_6H_5CO)_2S$. As mentioned in the experimental notes this gum like substnace was always formed and disappeared on standing.

EXPERIMENTAL WORK

Experiment I.

A round bottom one liter flask fitted with a three-hole rubber stopper was used. A glass tube conducted the chlorine into the mixture, the other tube was provided for the escape of HCl; a thermometer was placed in the third hole.

Five moles of glacial acetic acid, three fourths mole of sulfur monochloride were used. Chlorine was conducted into the mixture at 10° for eighteen hours, over a six day period; considerable excess chlorine was used. It was noticed that the red color of the SCl_2 was discharged upon the solution standing and reappeared upon leading chlorine into the mixture again. At the end of the chlorination the mixture was of a light yellow color.

The fractions (not weighed) were:

1 st	40 - 59°
2nd	60 - 120°
3rd	120 - 140°
4th	140 - 155°

S_2Cl_2 was found in fraction two and three. The method used being pouring a few drops of the liquid in ice water in which case free sulphur floats as a film. In later experiments the darkening of a bright copper wire when dipped in the liquid was the test generally used. An accident rendered quantative results worthless.

The boiling points of the possible compounds are:

Monochloracetyl chloride	50.9°
Monochloractic acid	106°
Dichloracetic acid	135-137°
Trichloracetic acid	195°
Dichloracetylchloride	107 - 108°
Acetic anhydride	137.9°
Sulphurmonochloride	138°
Sulphurdichloride	59°
Sulphurylchloride	69.2°

Experiment II

The light was screened from the chlorination flask in this experiment in order to ascertain if light was the catalyst which caused the decolorization of the mixture on standing.

The mixture used was 3 1/2 moles of CH_3CO_2H and 1/2 mole of S_2Cl_2, the temperature 8° - 10°. Chlorine was passed into the mixture for 16 hours over an interval of four days. The decolorization (due to SCl_2) was not prevented by excluding the light.

The mixture was fractionated in a two bulb column. The fractions were:

1 st fraction	40 - 60°	195 grams
2 nd ''	60 - 119°	46 grams
Tar-like residue		50 ''

The first cut on the basis CH_3COCl theoretical yield, showed a yield of 125 %; the SO_2Cl_2 found in the distillate e explained the overrun.

The presence of SO_2Cl_2 shown by pouring the mixture in H_2O:

$$SO_2Cl_2 \quad 2H_2O \qquad H_2SO_4 \quad HCl$$

The H_2SO_4 was proven by $BaCl_2$.

Experiment III.

The possiblility of an interaction between SO_2Cl_2, SCl_2 and CH_3CO_2H was studied. The hypothetical equation is

$$2\ CH_3CO_2H + SO_2Cl_2 + SCl_2 \longrightarrow 2\ CH_3COCl + 2SO_2 + 2HCl$$

Three and one half moles of CH_3CO_2H and one half mole of S_2Cl_2 were cooled to zero and saturated with Cl_2, one mole of SO_2Cl_2 was then added and the temperature allowed to rise to room temperature. After standing for thirty hours it was again distilled. The following cuts were made:

First fraction	40 - 55°	106 grams
Second ''	55 - 75°	109
Third ''	75 - 118°	55
Fourth ''	118 - 188°	53
Residue		68

A large portion of cuts one and two proved to be SO_2Cl_2.

Conclusion: Under the conditions of the experiment the interaction between SO_2Cl_2, S_2Cl_2 and CH_3CO_2H occured to only a slight extent.

Experiment IV

This experiment was made to determine the quality of the product formed when a large amount of SCl_4 was present.

Three and one half moles of CH_3CO_2H and one half mole of S_2Cl_2 were cooled as rapidly as possible without freezing out too much acetic acid down -19°. It was possible to cool down without entire solidification as the eutectic point was lowered by the formation of the chlorcompounds as chlorine was led into the mixture. The final cooling was done with $CaCl_2$ and ice. The mixture was saturated with Cl_2 at -19° and left well packed in salt and ice over night to permit the completion of the reaction.

$$SCl_4 + 2\ CH_3CO_2H \longrightarrow 2\ CH_3COCl + 2HCl + SO_2$$

The next day the mixture was again cooled to -17° and saturated with Cl_2. The mixture stood for 24 hours and was distilled.

First Cut 45° - 80° 133 grams

35% of the material boiled between 45 - 60°. No S_2Cl_2 was found in the distillate. Large amounts of SO_2Cl_2 were given off in distillation.

Second Cut 80 - 123° 42 grams

Ninety per cent boiled between 118° - 120°.

Weight of escaping gas and loss 50 grams

Weight of fractiona and residues recovered 290 grams.

A test was made on the third fraction by oxidizing with HNO_3 under a reflux, and H_2SO_4 was formed proving the presence of organic sulfur in this fraction.

Experiment VI

This experiment was made to obtain additional data regarding the possible reaction:

$$2CH_3CO_2H + SO_2Cl_2 + SCl_4 \longrightarrow 2CH_3COCl + 2SO_2 + 2HCl$$

One fourth mole of S_2Cl_2 and one half mole of SO_2Cl_2 were saturated with Cl_2 at 0° to -6° in order to change S_2Cl_2 to SCl_2.

Three moles of CH_3CO_2H was then added, the mixture was allowed to warm up in an ice salt bath to room temperature in twenty-four hours. It was again saturated with Cl_2 at 0o- 6° and left for twenty hours as before.

S_2Cl_2 and SCl_2 were absent in the mixture as shown by test. The mixture weighed 235 grams.

Weight of Distillate	40° - 80°	100 grams.
'' '' residue		125 ''
SO_2Cl_2 in distillate		59.27 ''

This shows 40.7% CH_3COCl formed in the first cut.

Conclusion : The reaction of SO_2Cl_2 and S_2Cl_2 with CH_3CO_2H is

not a practical one, altho an interesting possibility.

Experiment VII

This experiment was made to check data at 0° - 150°.

The mixture used was 3 1/2 moles of CH_3CO_2H

" " " " 1/2 mole of S_2Cl_2

The chlorination was carried on in diffused light. A very slow stream of chlorine was led into the mixture. Six hours of chlorination used up the S_2Cl_2.

The weight of the mixture was 305 grams

The weight of the first fraction 40° - 75° was 80 grams

" " " " " " 75 - 118° " 33 "

Two thirds of the 33 grams came over between 106° - 112° showing the presence of chloracetylchlorides.

Third Fraction 118° - 123° Acetic acid 68 grams

Fourth Fraction 123° - 150° 53 "

The loss due gas and volatility was 69 grams (305 - 236)

Conclusion: Under the conditions best suited to a commercial production the experiment shows a poor yield of CH_3COCl and a high formation of undesired higher chlor bodies.

Experiment VIII

Experiment made to determine the results to be expected at room temperature chlorination.

The proportions were the same as in the former experiments, viz: 3 1/2 moles of CH_3CO_2H and 1/2 mole of S_2Cl_2.

Chlorine was passed into the mixture slowly, the chlorination took ten hours, and occupied three days. The finished chlorinated mixture was allowed to stand at room temperature connected to a water cooled reflux condenser for twenty four hours to allow the escape of the gasses.

It was fractionate:

First Cut	30° - 80°	63 grams
Second ''	80° - 125°	27 ''
Third ''	125° - 140°	76 ''
Residue estimated		50 ''

SO_2Cl_3 found in first cut 42.1%

Conclusion: The fractions obtained do not show any very high increase in chloracetic or chloracetyl chloride at a higher temperature, but the yield of acetyl chloride is very low and tar residue high.

Experiment IX

This experiment was made to determine the effect of a higher concentration of S_2Cl_2 over the acetic present in the mixture.

One half mole of S_2Cl_2 was used and one mole of glacial acetic; the mixture was cooled to -5° to -12° while chlorine was passed into the mixture, until the evolution of HCl slowed down. Then 1/2 moles of additional CH_3CO_2H was added and Cl_2

passed in until the HCl given off became noticeably less, when another 1/2 mole of CH_3CO_2H was added. Unpon standing over night the SCl_2 color was completey discharged.

The mixture was fractionate:

First Fraction	30° - 75°	186 grams
Second ''	75° - 118°	8 ''
Third Fraction	118° - 125°	11 ''
Fourth ''	125° - 140°	not weighed
Fifth ''	140° - 175°	22 grams
Residue tar		

The fifth fraction gave a yield of 10 grams of monochlor acetic acid.

The first fraction was again fractionated in a column, 177- grams being taken.

First Cut	35 - 55°	126 grams
Residue in distilling flask		28 grams
		154 ''

Loss due to gas given off and volatility loss from the receiver 23 grams.

The % SO_2Cl_2 in the 126 grams cut was 37.2 %-- 36.9% This shows an indicated yield of 53.6% CH_3COCl on theory of CH_3CO_2H.

Conclusion: This experiment shows the most interesting possiblilities for the production of CH_3COCl from CH_3CO_2H. But the high % of SO_2Cl_2 makes the product obtained valueless.

Conclusion

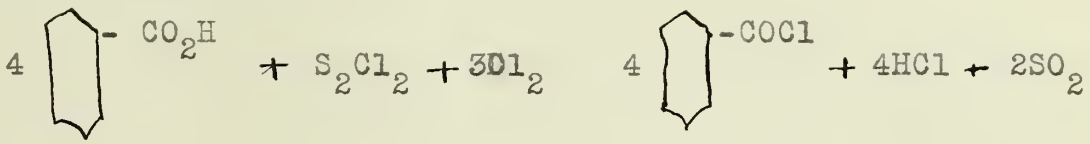
In as much as the problem was one in which the interest was largely in the practical possibilities of using S_2Cl_2 rather than PCl_3 as a chlorine carrier to produce acetyl chloride, it was proven impractical.

The yield of acetyl chloride in Experiments IV and IX are such as to make it profitable to produce acetyl chloride in this manner, provided a method may be devised to easily and cheaply remove the SO_2Cl_2 from the product. Experiment IV is of much less value as a practical method, owing to the low temperature at which the reaction was carried on; this objection does not hold for Experiment IX.

Experiment XI

The chlorination of Benzoic Acid to Benzoyl Chloride.

The chlorination was done at room temperature. Three hundred and fifty c.c. of CCl_4 was used as a solvent, or dilutent into which was charged 122 grams of benzoic acid (one mole) and i/3 mole of S_2Cl_2. The equation of the desired reaction being:



The rate of chlorination was very slow; many troublesome stoppages of the chlorination tube was caused by a gum-like deposit which formed in and about the inlet tube. After several attemts the experiment was discontinued.

Experiment XII

This experiment was also made using CCl_4 as a dilutent sovent, 350 c.c. being used. The benzoic acid was added in small portions in order to prevent the fomation of the gum-like material. After 17 grams had been added the gum-like substance prevented further admission of Cl_2. Very little HCl was given off at the time and evidence showed very little chlorination.

Experiment XIII

The solvent dilutent chsen in this experiment was benzoyl

chloride, as it was thought that the presence of the benzoyl chloride might act as a catalyst. One hundred and thirty-seven grams of benzoyl chloride and 1/8 mole (17 grams) of S_2Cl_2 were placed in the flask; the benzoic acid was added in ten-gram portions during an interval of eight days. The absorption of chlorine was very slow. The time during which chlorination was extended was thirty-four hours, chlorine being conducted into the solution for this time.

The disappearace of the benzoic acid from the mixture was taken as an indication of its chlorination. Sixty grams of benzoic acid were used.

The mixture was distilled, a large amount of HCl being given off, up to 150°.

First fraction	190°-195°	weighed	109 grams
Second ''	195°-205°	''	56 grams
Tar-like residue			53 ''

Deducting the original amount of benzoyl chloride added the yield was 28 grams or 43.4% of the crude material.

Boiling point	Benzoyl chloride	199°
Boiling point	Benzoic anhydride	360°

Conclusion

The chlorination of benzoic acid at room temperatures using S_2Cl_2 as a carrier is not a practical thing. The Experiment XIII showed the yield and the very slow rate of chlorination to make it an unprofitable thing under the conditions of the experiment. Other lines of research were taken up and the possible chlorination of benzoid acid using S_2Cl_2 as a carrier at higher temperatures was not tried.

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